SPECTROSCOPIC IMPLICATIONS OF A NEW THREE DIMENSIONAL MODEL OF THE OH STRETCH/TORSION POTENTIAL FOR HOONO AND DOONO

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Peroxy nitrous acid (or HOONO) is a molecule that has received considerable attention over recent years. Several groups have developed two-dimensional potential surfaces that include the HOON torsion and the OH stretch, as these appear to be the modes that are needed to describe the recorded action spectra in the $2v_{\mathrm{OH}}$ spectral region.[a,b] In its minimum energy structure, HOONO is in a planar conformation with an intramolecular hydrogen bond between the terminal hydrogen and oxygen atoms. This hydrogen bond leads to strong potential couplings between the HOON and OONO torsions near the potential minimum.

In the present study, we investigated the impacts of coupling between the two torsions on the energy levels, wave functions and predicted spectra of HOONO and DOONO. The calculations of the potential surface were carried out at the CCSD(T)/cc-pvtz and the dipole surface was evaluated using the QCISD/aug-cc-pvtz level of theory/basis. The resulting surfaces were fit to analytical functional forms and were then used to compute the vibrational wave functions, energies and transition intensities. We find that the importance of states that are localized near the so-called cis-perp-shelf on the HOONO potential, in which the OONO are planar and in a cis conformiation and the OH bond is roughly perpendicular to the OONO plane, has increased with the introduction of motion along the OONO torsion.

[a] A. B. McCoy, J. S. Francisco, J. L. Fry, A. K. Mollner, and M. Okumura *J. Chem. Phys.* **122**, 104311 (2005).
[b] J. Matthews and A. Sinha *J. Chem. Phys.* **122**, 104313 (2005).